(19)日本国特許庁 (JP)

## (12) 公開特許公報(A)

(川)特許出顧公開登号 特開2002-180264 (P2002-180264A)

(43)公開日 平成14年6月26日(2002.6.26)

(51) Int.CL.7

級別記号

FΙ

テーマコード(参考)

C28C 22/52

22/83

C23C 22/52

4K026

22/83

審査請求 未請求 請求項の数3 OL (全3 頁)

(21)出願番号

物類2000-379434(P2000-379434)

(71) 出廢人 592193432

有限会社杉本第色所

(22)出願日

平成12年12月13日(2000.12.13)

常山與高岡市戸出來町39-6

(72) 死明者 杉本 敏弘

官山県高岡市戸出祭町39番6号 有限会社

杉本着各所內

(74)代理人 100114074

**介理士 大谷 嘉一** 

Fターム(参考) 4K028 AAG6 BA13 BB01 CA16 IN92

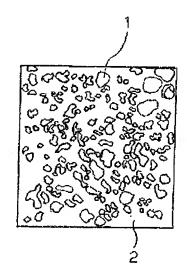
DAUS EAOS EBO2

#### (54) 【発明の名称】 縁寄色斑点模様の鋼板及びその処理方法

#### (57)【要約】

【課題】 大型で薄い銅又は銅台金板に対して熱ひずみや 熱変形を防止すべく常温において、化学的に容易に着色 処理が出来、着色皮膜の密着性及び耐久性に優れ、天然 緑青色に近い高級感のある緑青色斑点模様の形成及び、 そのようにして得られた銅板の提供を目的とする。

【解疾手段】銅板の表面に化学的に緑青色斑点模様を形成する暮色方法において、銅板の表面をセレンを含有する酸性水溶液にて1次黒染処理し、炭酸塩又は、及び、塩化塩を含有する酸性水溶液にて下地緑青処理し、その後に酸洗浄し、当該セレンを含有する酸性水溶液にて2次黒染処理し、その後に炭酸塩又は、及び、塩化塩を含有する酸性水溶液を当該銅板の表面に噴霧して緑青色斑点模様を形成した。また必要に応じてスプレー後に布等でバッテングした。



h

ge g f

# PATENT ABSTRACTS OF JAPAN

(11)Publication number:

2002-180264

(43) Date of publication of application: 26.06.2002

(51)Int.CI.

C23C 22/52 C23C 22/83

(21)Application number : 2000-379434

(71)Applicant : SUGIMOTO

CHIYAKUSHIYOKUSHIYO:KK

(22)Date of filing:

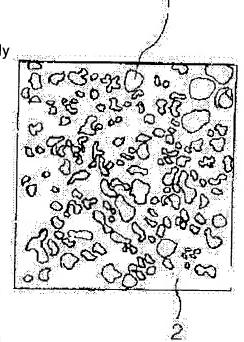
13.12.2000

(72)Inventor: SUGIMOTO TOSHIHIRO

# (54) COPPER SHEET WITH PATINA-COLORED DOTTED PATTERN AND TREATMENT **METHOD THEREFOR**

### (57)Abstract:

PROBLEM TO BE SOLVED: To form a patina-colored dotted pattern of which coloring treatment can chemically and easily performed to a large and thin copper or copper alloy sheet at ordinary temperature so as to prevent thermal strain and thermal deformation, has excellent adhesion and durability of a colored film, and imparts a noble feeling close to that in a natural patina color, and a steel sheet obtained in this way. SOLUTION: The patina-colored dotted pattern is chemically formed on the surface of a copper sheet. In this coloring method, the surface of the copper sheet is subjected to primary blackening treatment with an acidic aqueous solution containing selenium, and is subjected to base patina treatment with an acidic aqueous solution



containing carbonate or/and chloride. After that, the copper sheet is subjected to acid cleaning, and is subjected to secondary blackening treatment with the acidic aqueous solution containing selenium. After that, the surface of the copper sheet is sprayed with an acid aqueous solution containing carbonate or/and chloride to form a patina-colored dotted pattern. If required, after the spraying, a patting is performed thereto with a cloth or the like.

Japan Patent Office is not responsible for any damages caused by the use ( this translation.

1. This document has been trar precisely.

2.\*\*\*\* shows the word wh;

3.In the drawings, any wc

r computer. So the translation may not reflect the original

translated.

### **CLAIMS**

[Claim(s)]

[Claim 1] The copper plate in the front face of a copper plate in the forms a copper rust colored spot point after that in a carbonate or the aqueous acreobtained.

colored spot point pattern characterized by processing the is containing a selenium in the coloring approach which hemically on the surface of a copper plate, processing hich reaches and contains a chlorination salt, and being

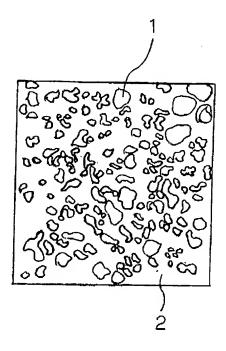
[Claim 2] In the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, primary blackening of the front face of a copper plate is carried out in the aqueous acids containing a selenium. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or the copper plate of the copper rust colored spot point pattern characterized by spraying the aqueous acids which reach and contain a chlorination salt on the front face of the copper plate concerned, and being obtained.

[Claim 3] In the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, primary blackening of the front face of a copper plate is carried out in the aqueous acids containing a selenium. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or the copper plate of the copper rust colored spot point pattern characterized by the front face of the copper plate concerned and being obtained in the PATTENGU member to which the aqueous acids which reach and contain a chlorination salt were made to sink in or adhere.

[Translation done.]

# **BEST AVAILABLE COPY**

Drawing selection Representative drawing



Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Field of the Invention] This invention relates to the copper plate which made the copper rust colored spot point pattern form in the front face of copper or a copper alloy plate chemically, and its art. [0002]

[Description of the Prior Art] It is known widely that the precise copper rust coat by which poor solubility was stabilized in water by prolonged contact for the atmospheric-air component which contains moisture on the surface of copper will be obtained. Various examination of acquiring a copper rust colored spot point pattern from such a copper rust color appearance having the sophisticated-design effectiveness simply artificially is carried out.

[0003] For example, the conventional artificial copper rust approach holds what carried out the chemical treatment to the copper front face by the heat-and-high-humidity environment. However, by such approach, there was also a problem which will deform if forming only the processor which holds a tabular big product by such environment itself applies heat to tabular copper or a tabular copper alloy plate difficult.

[0004] Moreover, although the approach of carrying out paint of the different color tone and different shade on it to the substrate pattern which performed copper rust color paint, and forming a copper rust colored spot point pattern was proposed, the adhesion of a paint film was bad and it was difficult for a problem to have been in endurance and to have made the copper rust color of the nature also in appearance resemble.

[0005]

[Problem(s) to be Solved by the Invention] In view of the above technical problems, that a heat strain and heat deformation should be prevent to large-sized and thin copper or a copper alloy plate, this invention can perform coloring processing easily chemically in ordinary temperature, be excellent in the adhesion and endurance of a coloring coat, and aim at formation of a copper rust colored spot point pattern with the high-class feeling near a natural copper rust color, and offer of a copper plate obtained by make it such.

[0006]

[Means for Solving the Problem] Invention according to claim 1 processed the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, and it considered as the copper plate of the copper rust colored spot point pattern characterized by the carbonate or being processed and obtained in the aqueous acids which reach and contain a chlorination salt after that.

[0007] in order for the aqueous acids which contain a selenium here to mean the water solution of the oxidizing quality contained 0.3 - 3% of selenious acids, to melt and prepare a selenium dioxide etc. in water and to stabilize blackening of the front face of a copper plate -- a copper sulfate -- 0.1 - 3% -- or -and you may add 0.1 - 1% of sulfuration salts. A front face will be colored a black system if a copper plate etc. is immersed in the aqueous acids (henceforth a black-oxide-finish water solution) containing

such a selenium. It rinsed after that and the front face was dried.

[0008] Moreover, especially if it says a carbonate or that the aqueous acids which reach and contain a chlorination salt contain salts, such as an ammonium carbonate and an ammonium chloride, it reacts with a black coat and basic copper salt is formed, it will not be limited, but it reaches and a carbonate or the thing which melted the chlorination salt ten to 50 g/l, respectively is said to the water solution which diluted the aqueous acids containing the selenium for the above-mentioned black oxide finish 10 to 20 times with water. It reaches, and if surface treatment is carried out in such a carbonate or the aqueous acids (henceforth a copper rust water solution) containing a chlorination salt, a copper rust love scene will be formed on the surface of a copper plate.

[0009] Invention according to claim 2 carries out primary blackening of the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or it reached and considered as the copper plate of the copper rust colored spot point pattern characterized by spraying the aqueous acids containing a chlorination salt on the front face of the copper plate concerned, and being obtained. Although a copper rust colored spot point pattern can be formed also by the approach according to claim 1, the \*\*\*\*\*\* of a coloring coat is ensured, and in order to make the copper rust colored spot point pattern which has a high-class feeling more form, invention according to claim 2 is made.

[0010] Preliminary washing of the front faces, such as a copper plate, was carried out in the dilution sulfuric-acid water solution etc., primary blackening was carried out in the black-oxide-finish water solution after rinsing, substrate copper rust processing was carried out in the copper rust water solution after rinsing desiccation, pickling was carried out in the dilution sulfuric-acid water solution after desiccation and rinsing, secondary blackening was carried out after rinsing, the copper rust water solution was used for the front face for the spray gun for paint etc. after rinsing and desiccation, and the spray was carried out. Then, while the waterdrop by which the spray was carried out reacts to a front face partially, since it dries, a copper rust colored spot point pattern is formed. Therefore, if it repeats twice or more, taking a desiccation process for a copper rust water solution if needed, the copper rust colored spot point pattern more near nature will be formed.

[0011] Invention according to claim 3 carries out primary blackening of the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or it considered as the copper plate of the copper rust colored spot point pattern characterized by the front face of the copper plate concerned and being obtained in the PATTENGU member to which the aqueous acids which reach and contain a chlorination salt were made to sink in or adhere. PATTENGU [ this ] so that a front face might be lightly struck using the PATTENGU member which instead absorbs copper rust water solutions, such as cloth and sponge, in addition to the process which carries out the spray of the copper rust water solution in invention according to claim 2. When done in this way, the remains of PATTENGU carried out an appearance like \*\*\*\* produced naturally the degree.

[0012] Thus, after making a copper rust colored spot point pattern form on the surface of a copper plate, it finished by carrying out clear paint.

[0013]

[Embodiment of the Invention] The gestalt of desirable operation of this invention is explained hereafter, the black-oxide-finish water solution which pickled the copper plate of the thin shape of a sheet with a thickness of 0.1-0.4mm for about 1 minute in the dilution sulfuric-acid water solution 1 to 5%, and diluted 3% of selenic-acid water solution about 4 times after rinsing -- ordinary temperature -- primary blackening during about 5 - 6 minutes was carried out. Then, it rinsed and dried, and water was

immersed in about 100ml of black-oxide-finish water solutions of the same concentration as the above at about 1000ml, in addition the copper rust water solution which diluted, and melted and prepared 20g of ammonium carbonates, and 30g of ammonium chlorides, and substrate copper rust processing was carried out. Next, rinsing preliminary washing was carried out after desiccation, acid cleaning was carried out in the dilution sulfuric-acid water solution, and secondary blackening was performed for about 10 minutes after rinsing. The spray of the copper rust water solution prepared to the concentration same with having used for the above-mentioned substrate copper rust on the front face rinsed and dried after this blackening was carried out. After the copper rust water solution which carried out the spray to the 1st time dried, when it was made to dry by carrying out the 2nd spray, the copper rust spot pattern that a mimetic diagram was shown in drawing 1 was formed again.

[0014] The 1st above-mentioned spray was carried out similarly, carried out the 2nd spray using the old liquid which carried out copper rust processing last time, and it wiped off so that it might strike using a cloth towel etc. Thereby, the copper rust pattern as shown in <u>drawing 2</u> was formed. Moreover, when it wiped off so that copper rust processing of after that still older liquid might be included in a PATTENGU member and might be struck strongly, a pattern that the copper rust part as shown in <u>drawing 3</u> became thin was formed.

[0015]

[Effect of the Invention] According to the copper rust colored spot point encaustic formation approach by the chemical preparation concerning this invention, since it can process in ordinary temperature, there is no heat deformation, and not only heavy-gage ingredients, such as a casting used as a copper base material like before, but the copper plate of the shape of a thin sheet etc. can be processed easily. Moreover, after carrying out primary black oxide finish and substrate copper rust processing, secondary black oxide finish is carried out, and if copper rust color processing is carried out, the adhesion to the copper plate of chemical conversion coatings will become what was very excellent.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### TECHNICAL FIELD

[Field of the Invention] This invention relates to the copper plate which made the copper rust colored spot point pattern form in the front face of copper or a copper alloy plate chemically, and its art.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### **MEANS**

[Means for Solving the Problem] Invention according to claim 1 processed the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate, and it considered as the copper plate of the copper rust colored spot point pattern characterized by the carbonate or being processed and obtained in the aqueous acids which reach and contain a chlorination salt after that.

[0007] in order for the aqueous acids which contain a selenium here to mean the water solution of the oxidizing quality contained 0.3 - 3% of selenious acids, to melt and prepare a selenium dioxide etc. in water and to stabilize blackening of the front face of a copper plate -- a copper sulfate -- 0.1 - 3% -- or -and you may add 0.1 - 1% of sulfuration salts. A front face will be colored a black system if a copper plate etc. is immersed in the aqueous acids (henceforth a black-oxide-finish water solution) containing such a selenium. It rinsed after that and the front face was dried.

[0008] Moreover, especially if it says a carbonate or that the aqueous acids which reach and contain a chlorination salt contain salts, such as an ammonium carbonate and an ammonium chloride, it reacts with a black coat and basic copper salt is formed, it will not be limited, but it reaches and a carbonate or the thing which melted the chlorination salt ten to 50 g/l, respectively is said to the water solution which diluted the aqueous acids containing the selenium for the above-mentioned black oxide finish 10 to 20 times with water. It reaches, and if surface treatment is carried out in such a carbonate or the aqueous acids (henceforth a copper rust water solution) containing a chlorination salt, a copper rust love scene will be formed on the surface of a copper plate.

[0009] Invention according to claim 2 carries out primary blackening of the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or it reached and considered as the copper plate of the copper rust colored spot point pattern characterized by spraying the aqueous acids containing a chlorination salt on the front face of the copper plate concerned, and being obtained. Although a copper rust colored spot point pattern can be formed also by the approach according to claim 1, the \*\*\*\*\*\* of a coloring coat is ensured, and in order to make the copper rust colored spot point pattern which has a high-class feeling more form, invention according to claim 2 is made.

[0010] Preliminary washing of the front faces, such as a copper plate, was carried out in the dilution sulfuric-acid water solution etc., primary blackening was carried out in the black-oxide-finish water solution after rinsing, substrate copper rust processing was carried out in the copper rust water solution after rinsing desiccation, pickling was carried out in the dilution sulfuric-acid water solution after desiccation and rinsing, secondary blackening was carried out after rinsing, the copper rust water solution was used for the front face for the spray gun for paint etc. after rinsing and desiccation, and the spray was carried out. Then, while the waterdrop by which the spray was carried out reacts to a front face partially, since it dries, a copper rust colored spot point pattern is formed. Therefore, if it repeats

twice or more, taking a desiccation process for a copper rust water solution if needed, the copper rust colored spot point pattern more near nature will be formed.

[0011] Invention according to claim 3 carries out primary blackening of the front face of a copper plate in the aqueous acids containing a selenium in the coloring approach which forms a copper rust colored spot point pattern chemically on the surface of a copper plate. A carbonate It reaches, and in the aqueous acids containing a chlorination salt, substrate copper rust processing is carried out, acid cleaning is carried out after that, and secondary blackening is carried out in the aqueous acids containing the selenium concerned. After that Or a carbonate Or it considered as the copper plate of the copper rust colored spot point pattern characterized by the front face of the copper plate concerned and being obtained in the PATTENGU member to which the aqueous acids which reach and contain a chlorination salt were made to sink in or adhere. PATTENGU [ this ] so that a front face might be lightly struck using the PATTENGU member which instead absorbs copper rust water solutions, such as cloth and sponge, in addition to the process which carries out the spray of the copper rust water solution in invention according to claim 2. When done in this way, the remains of PATTENGU carried out an appearance like \*\*\*\* produced naturally the degree.

[0012] Thus, after making a copper rust colored spot point pattern form on the surface of a copper plate, it finished by carrying out clear paint.

[0013]

[Embodiment of the Invention] The gestalt of desirable operation of this invention is explained hereafter, the black-oxide-finish water solution which pickled the copper plate of the thin shape of a sheet with a thickness of 0.1-0.4mm for about 1 minute in the dilution sulfuric-acid water solution 1 to 5%, and diluted 3% of selenic-acid water solution about 4 times after rinsing -- ordinary temperature -- primary blackening during about 5 - 6 minutes was carried out. Then, it rinsed and dried, and water was immersed in about 100ml of black-oxide-finish water solutions of the same concentration as the above at about 1000ml, in addition the copper rust water solution which diluted, and melted and prepared 20g of ammonium carbonates, and 30g of ammonium chlorides, and substrate copper rust processing was carried out. Next, rinsing preliminary washing was carried out after desiccation, acid cleaning was carried out in the dilution sulfuric-acid water solution, and secondary blackening was performed for about 10 minutes after rinsing. The spray of the copper rust water solution prepared to the concentration same with having used for the above-mentioned substrate copper rust on the front face rinsed and dried after this blackening was carried out. After the copper rust water solution which carried out the spray to the 1st time dried, when it was made to dry by carrying out the 2nd spray, the copper rust spot pattern that a mimetic diagram was shown in drawing 1 was formed again.

[0014] The 1st above-mentioned spray was carried out similarly, carried out the 2nd spray using the old liquid which carried out copper rust processing last time, and it wiped off so that it might strike using a cloth towel etc. Thereby, the copper rust pattern as shown in <u>drawing 2</u> was formed. Moreover, when it wiped off so that copper rust processing of after that still older liquid might be included in a PATTENGU member and might be struck strongly, a pattern that the copper rust part as shown in <u>drawing 3</u> became thin was formed.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### **DESCRIPTION OF DRAWINGS**

[Brief Description of the Drawings]

Drawing 1] The example in the condition of having formed the spot pattern by the spray is shown.

Drawing 2] The example in the condition of having formed the spot pattern in PATTENGU is shown.

[Drawing 3] The example in the condition of having formed the spot pattern in strong PATTENGU is shown.

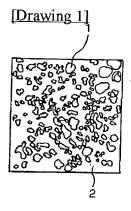
[Description of Notations]

- 1 A Part for Copper Rust Color Part
- 2 Part of Blackish Color Tone
- 3 Part of Color Tone of Tea System

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### **DRAWINGS**



[Drawing 2]



[Drawing 3]

